Interactions of TICs/CWAs with Activated Carbon ASZM-TEDA Impregnants: a Theoretical Investigation

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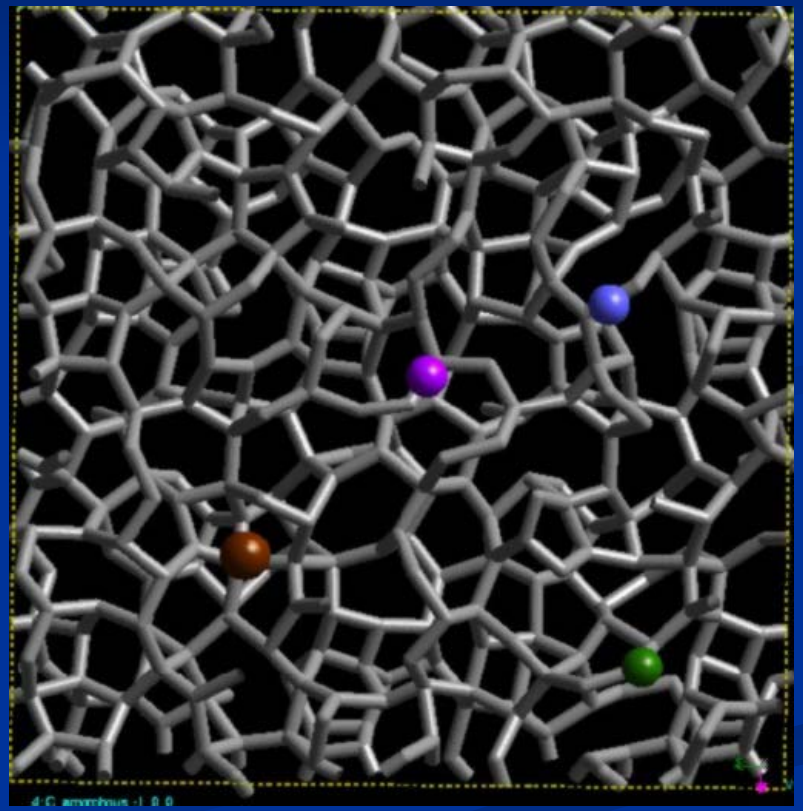
Filtration of Toxic Industrial Chemicals

- Current filtration technology involves use of ASZM-TEDA: activated carbon impregnated with Cu, Zn, Ag, Mo, and TEDA (triethylenediamine).
- The role of the individual components is poorly understood.
- There is experimental evidence of synergistic effects (and interference)
- Poisoning?
- Environmental effects? Humidity?
- Selectivity?

Target compounds include: HCN, ClCN, NCCN, HCl, $COCl_2$, Cl_2



Phosgene Decomposition by Zinc Ion

3 Pathways have been previously studied *

$Zn^{2+} + COCl_2 \longrightarrow ZnCl^{+} + COCl^{+}$ *path 1*

$\longrightarrow Zn^{2+}[O{=}CCl_2]$ *path 2*

$\longrightarrow [Cl_2ZnCO]^{2+}$ *path 3*

* E. Fattal and E.A. Carter *J. Phys. Chem A* **2000**, *104*, 2248-2252

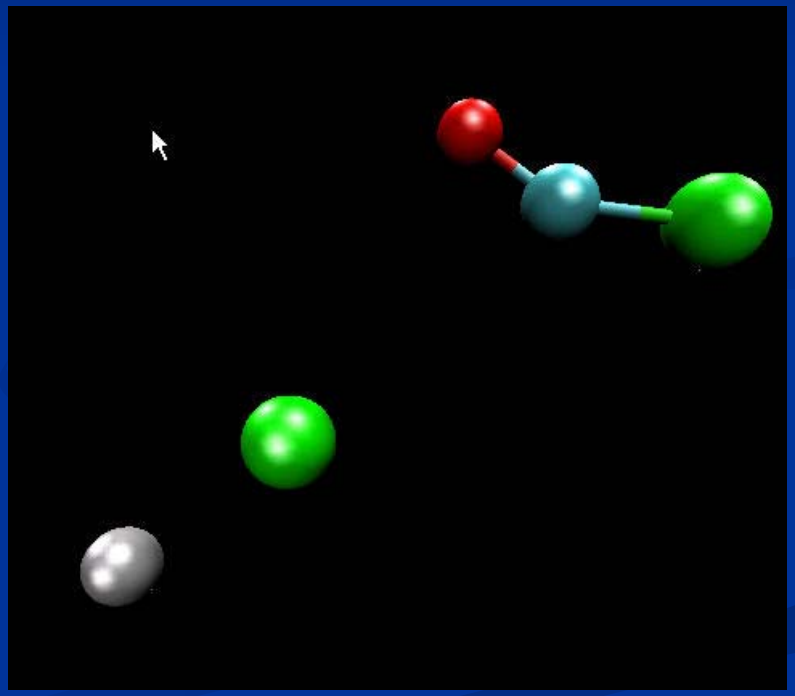
Phosgene + Zinc Energetics Review

ΔE (products – reactants) (kcal/mol)

Carter CASSCF (10/10)/MRSCCI -174.0

Path 1	3-21G*	6-31G**	6-311+G
RHF	-175.7	-172.8	-171.9
MP2	-193.4	-187.6	-195.5
QCISD	-196.9	-186.4	-191.9

	MP2/6-31G**	Carter
Path 2	-107.9	-82
Path 3	-84.6	-67.2



Correct sequence predicted at a greatly reduced computational cost for gas phase reactions

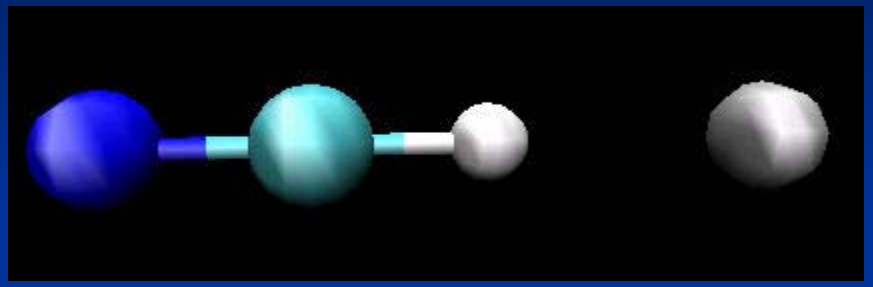
Phosgene + Zinc Path 1 geometries

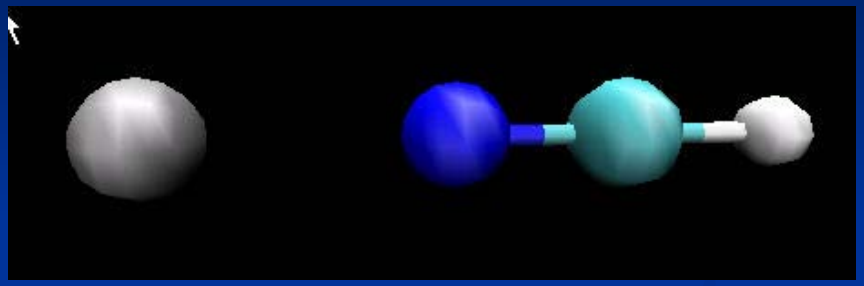
$Zn^{2+} + COCl_2 \longrightarrow ZnCl^+ + COCl^+$

		Carter	Current HF/3-21G* QCISD/6-311+G	Exp.
$COCl_2$	C-O (Å)	1.176	1.17 / 1.20	1.176
	C-Cl (Å)	1.738	1.74 / 1.83	1.738
	<Cl-C-Cl	111.80	112.18 / 111.9	111.83
$COCl^+$	C-O (Å)	1.114	1.11 / 1.14	
	C-Cl (Å)	1.629	1.57 / 1.66	
	<O-C-Cl	180.0	180.0 / 180.0	
ZnCl+	Zn-Cl (Å)	2.132	2.04 / 2.11	2.24

Cyanide Series: AC + Metal Ion

$HCN + Zn^{2+} \longrightarrow ?$





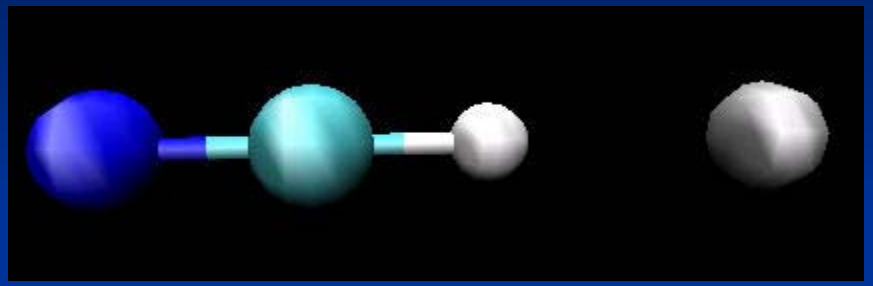
Metal ion	Theory/BS	NCH complex $\Delta E_{(prod-reac)}$ (kcal/mol)
Zn^{2+}	HF/6-31G**	-103.26
Zn^{2+}	HF/LANL2DZ	-110.15
Zn^{2+}	HF/6-311+G	-108.85
Zn^{2+}	B3LYP/6-31G**	-118.83
Zn^{2+}	MP2/6-31G**	-105.90

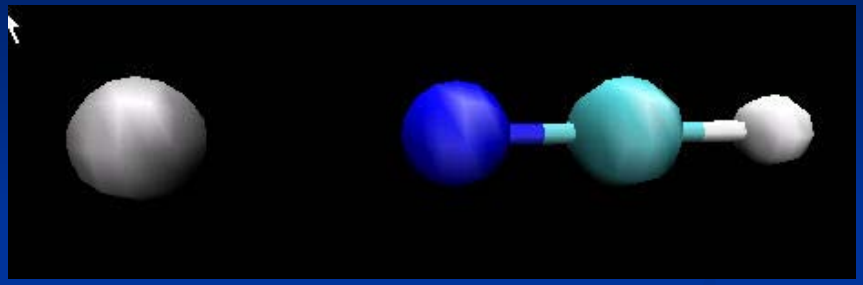
CP corrected
No stable HCN –end on complex found

Cyanide Series: AC + Metal Ion

$HCN + Cu^{2+} \longrightarrow ?$

$HCN + Cu^{1+} \longrightarrow ?$



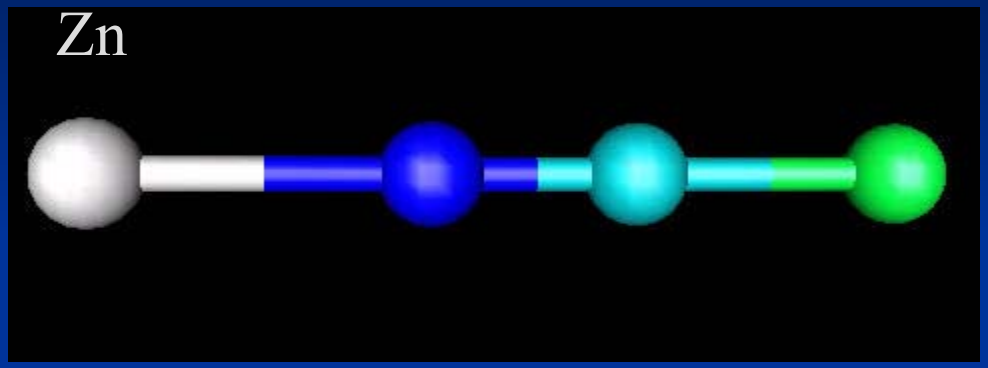


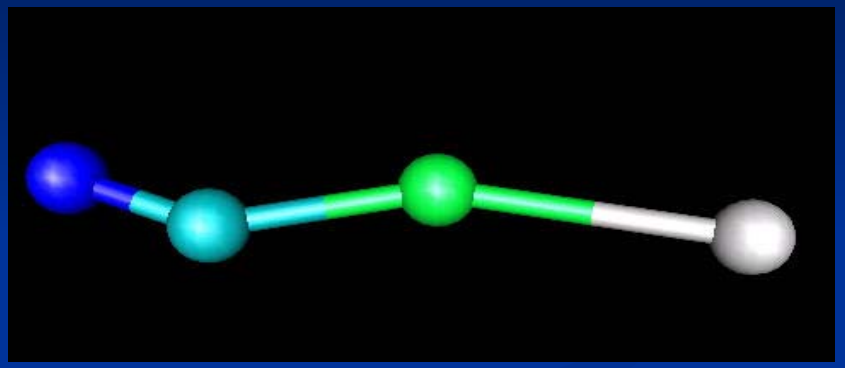
Metal Ion	Theory/BS	NCH complex $\Delta E_{(prod-reac)}$ (kcal/mol)
Cu^{2+}	HF/6-31G**	-111.58
Cu^{2+}	HF/6-31G* Pulay*	-93.18
Cu^{2+}	MP2/6-31G**	-117.36

**An Improved 6-31g* Basis Set for Transition Metals*
A.V. Mitin, J. Baker, P. Pulay *JCP* **118** p 7775 (2003)

Cyanide Series: CK + Zinc Ion

$$ClCN + Zn^{2+} \longrightarrow ?$$

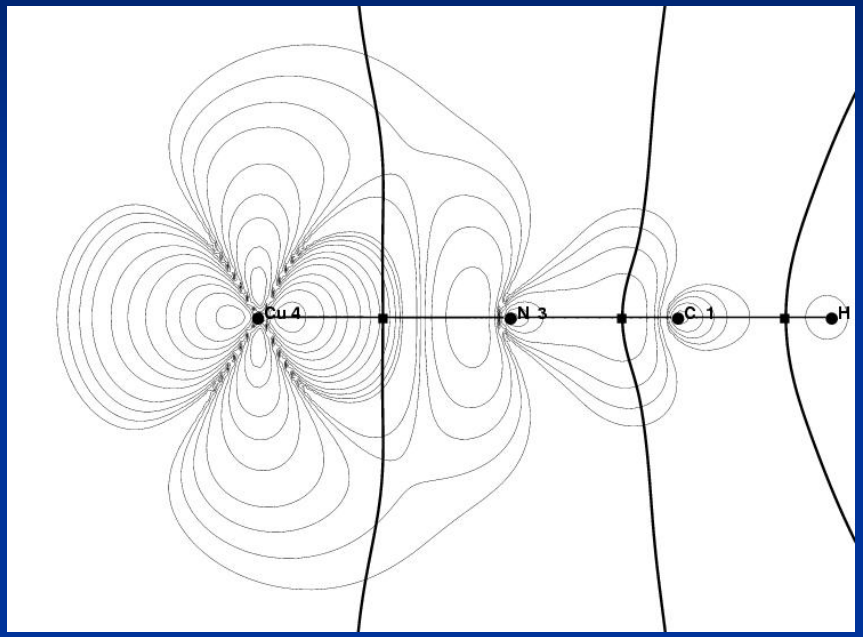




Theory/BS	$\Delta E_{(prod-reac)}$ (kcal/mol)
HF/6-31G**	-114.02
MP2/6-31G**	-116.30
QCISD/6-31G**	-115.63

CP corrected
N-end on

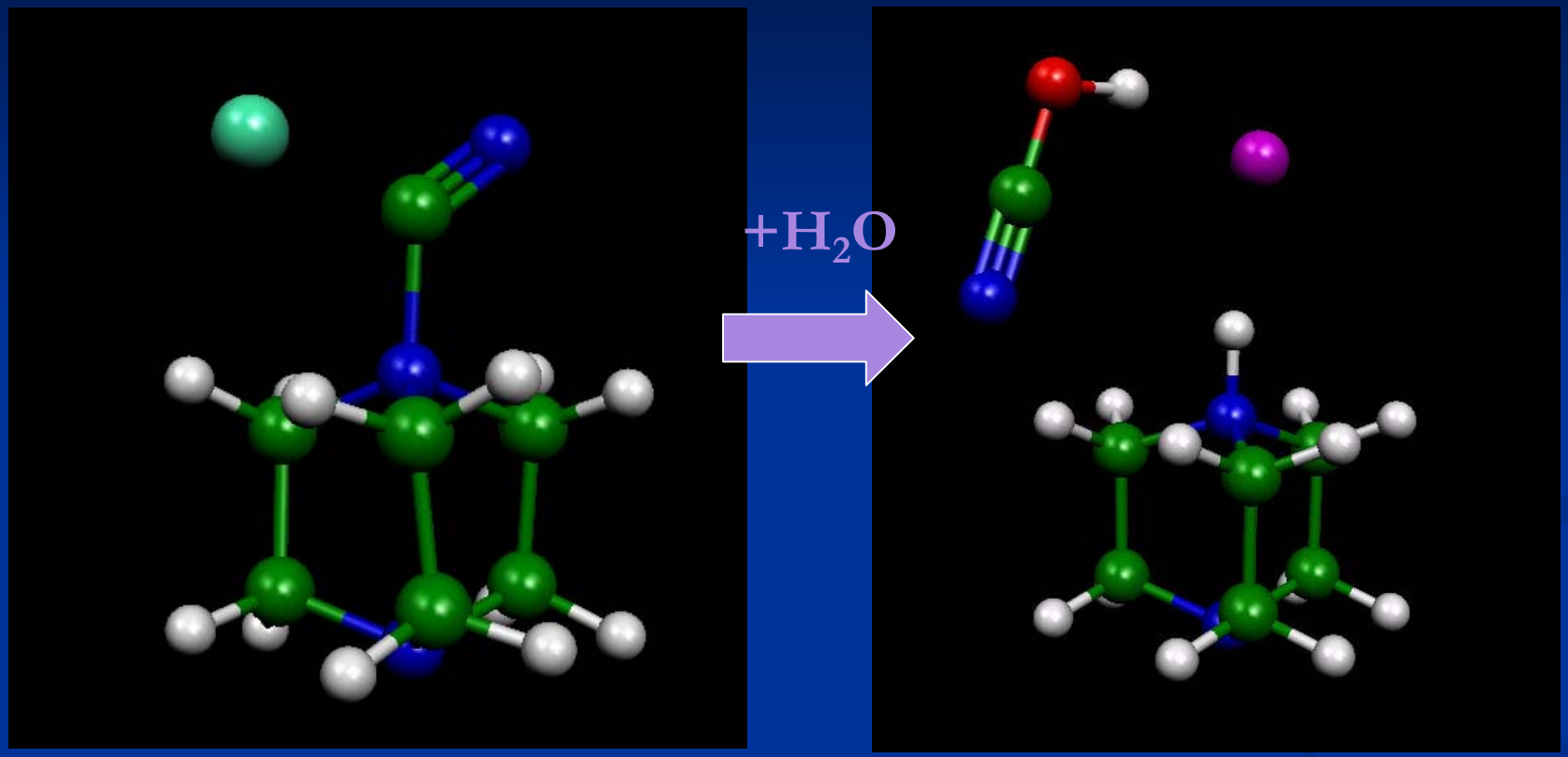
Cyanide Series: AIM Analysis



Atoms in Molecules (AIM) analysis as per Bader *Atoms in Molecules: A Quantum Theory* Oxford 1990

Metal	TIC	ρ	lap
Zn^{2+}	CK	0.12157	0.47824
Zn^{2+}	AC	0.10768	0.39185
Cu^{2+}	AC	0.14568	0.77601
Cu^{2+}	CK	0.10795	0.60587

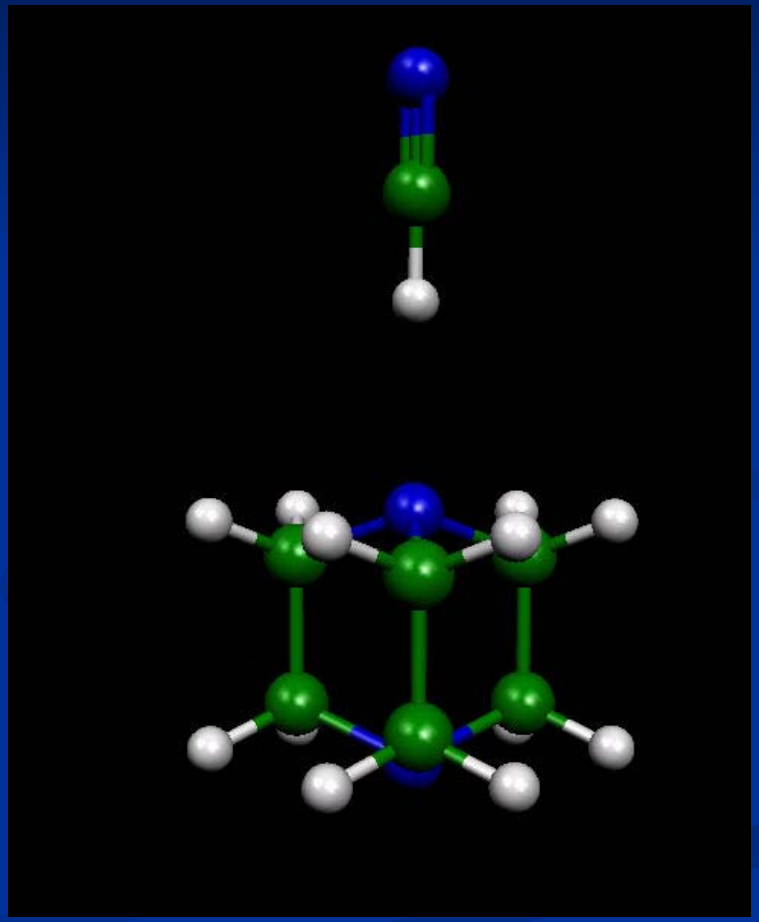
Cyanide Series: CK + TEDA complexes



TEDA binds CK and facilitates HCl formation, formation of HOCN in presence of water?
Synergy with metal ions?

Cyanide Series: AC + TEDA complexes

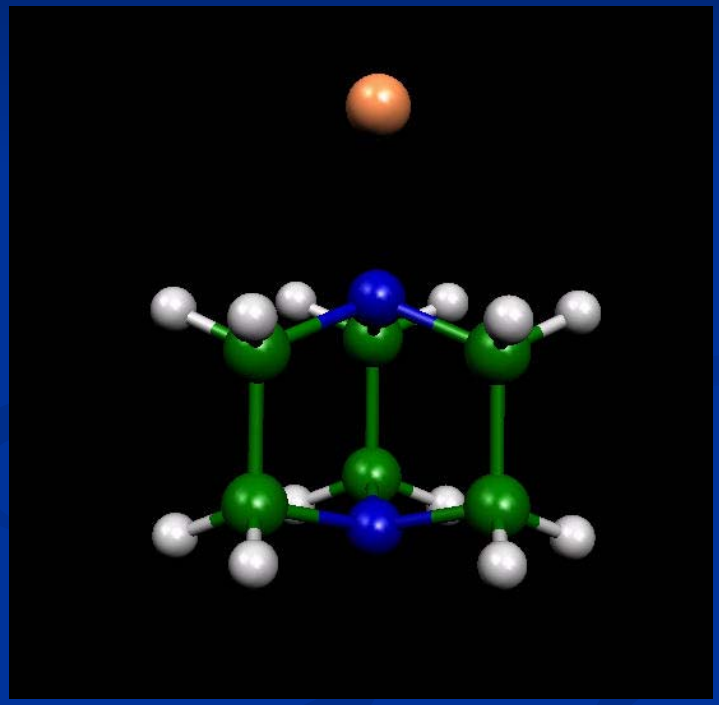
TIC	Theory/BS	$\Delta E_{(prod-reac)}$ (kcal/mol)
HCN	HF/6-31G**	-6.92
HCN	MP2/6-31G**	-9.63
HCl	HF/6-31G**	-8.77
HCl	MP2/6-31G**	-15.77



TEDA weakly binds HCN, HCl

Cyanide Series: Metal + TEDA complexes

Metal	Theory/BS	$\Delta E_{(prod-reac)}$ (kcal/mol)
Zn^{2+}	HF/6-31G**	-144.21
Zn^{2+}	MP2/6-31G**	-171.53
Cu^{2+}	HF/6-31G**	-143.93
Cu^{2+}	MP2/6-31G**	-226.45



Strong binding of both metals to TEDA

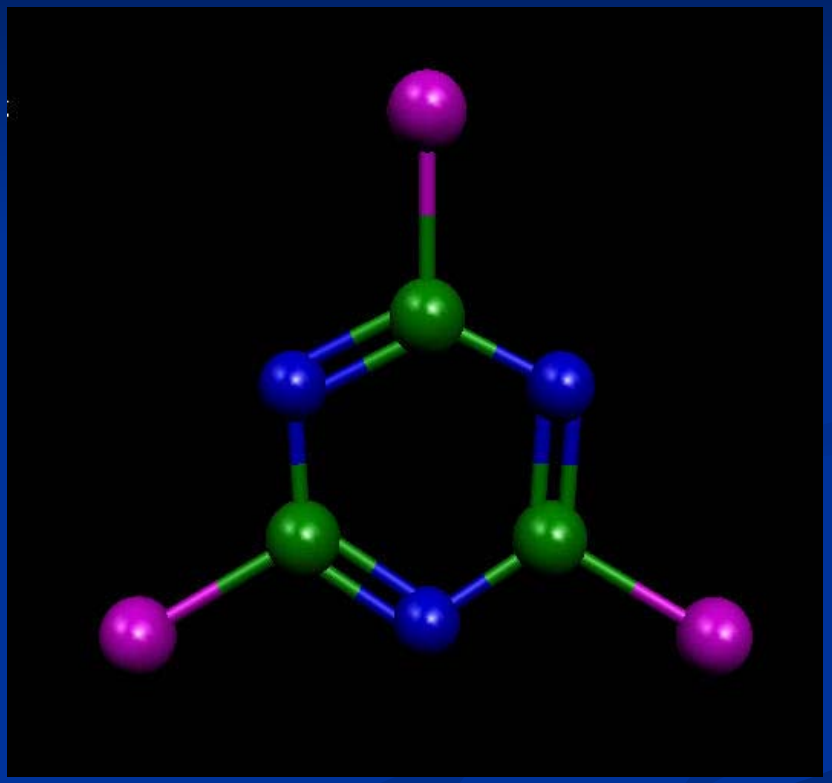
Cyanide Series/Metal Ion Interactions

CK polymerization:

3 CK -> $C_3N_3Cl_3$ (cyanuric chloride)

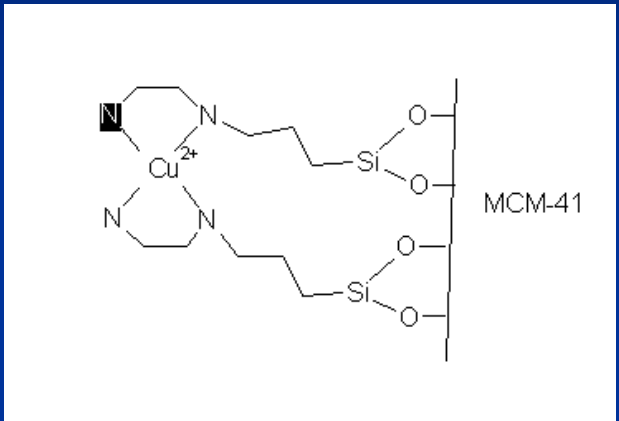
Energetically favorable in gas phase as per previous theory and expt (Pai et al, JPCA **1997**, *101*, 3400-3407, Kharasch et al, Ind. and Eng. Chem. **1949**, *41*, 2840-2842)

Catalyzed by TM?

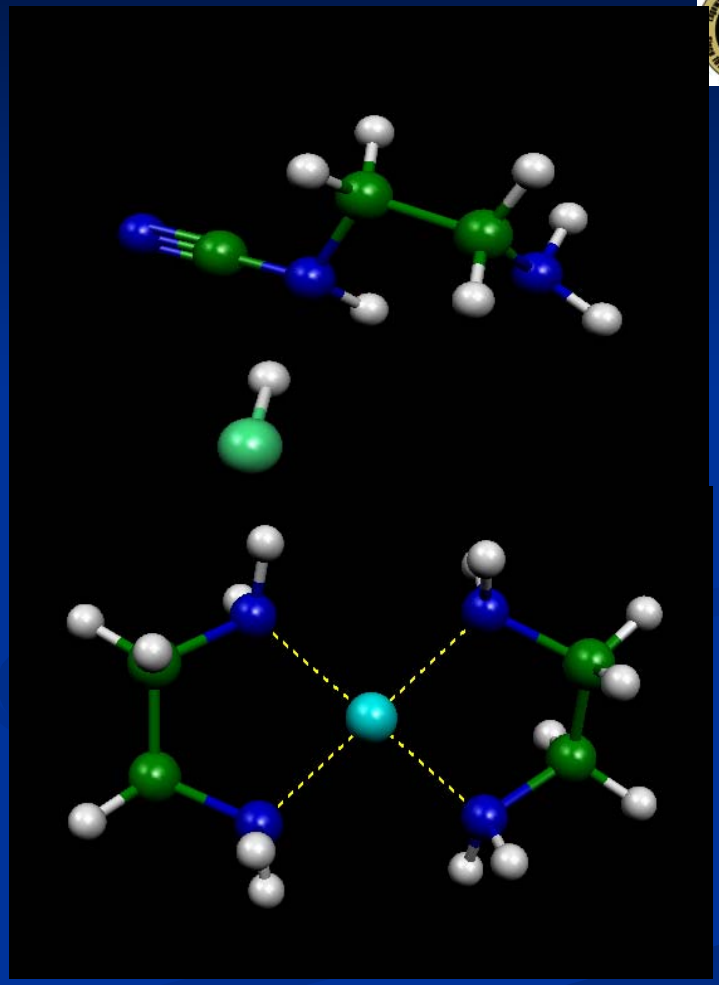


Alternative Formulation: Si-based

Free amine will break down CK



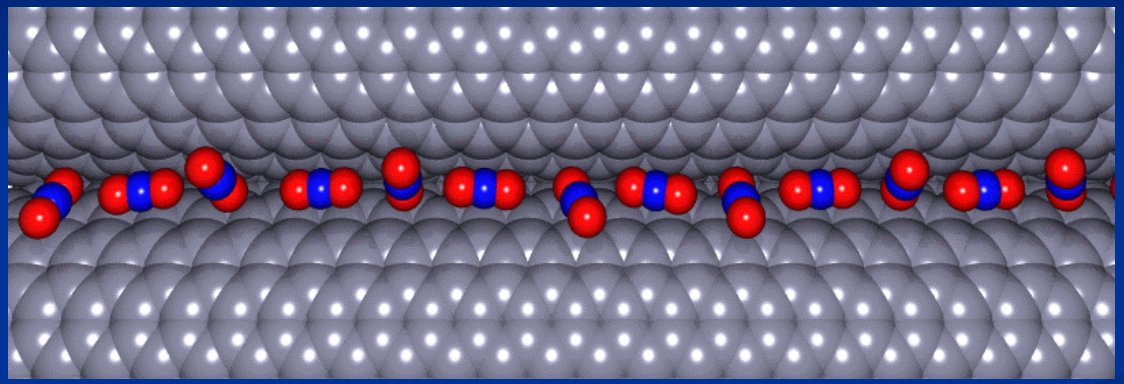
Cu-complexed-amine will not



Diamine – Cu silicate-based formulation of Brown group Hudderfield, UK *J. Mater. Chem.*, 2002, **12**, 1086-1089

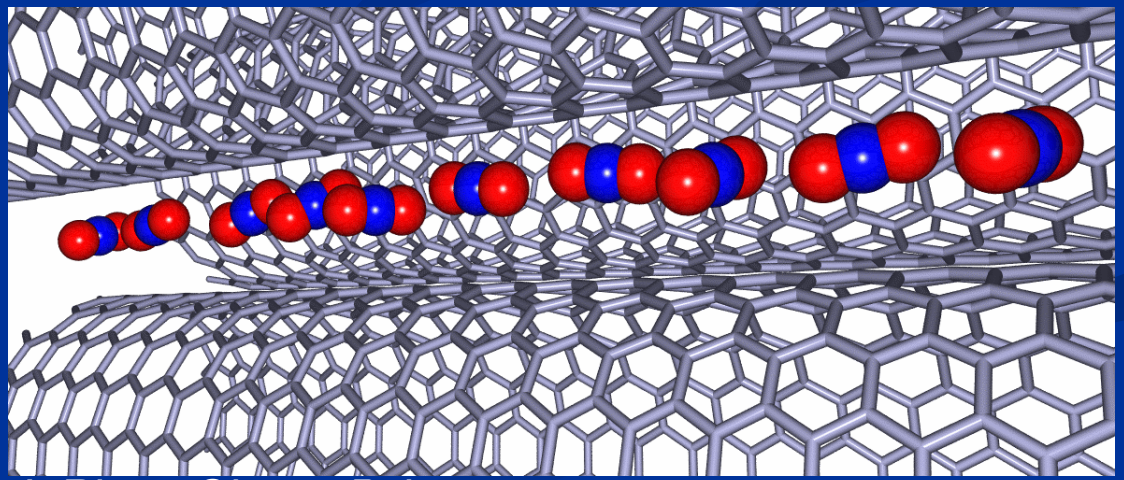
Snapshots

Classical Model Potential Grand Canonical Monte Carlo Calculations at 77 K



Top:

CO_2 adsorption in a single groove site

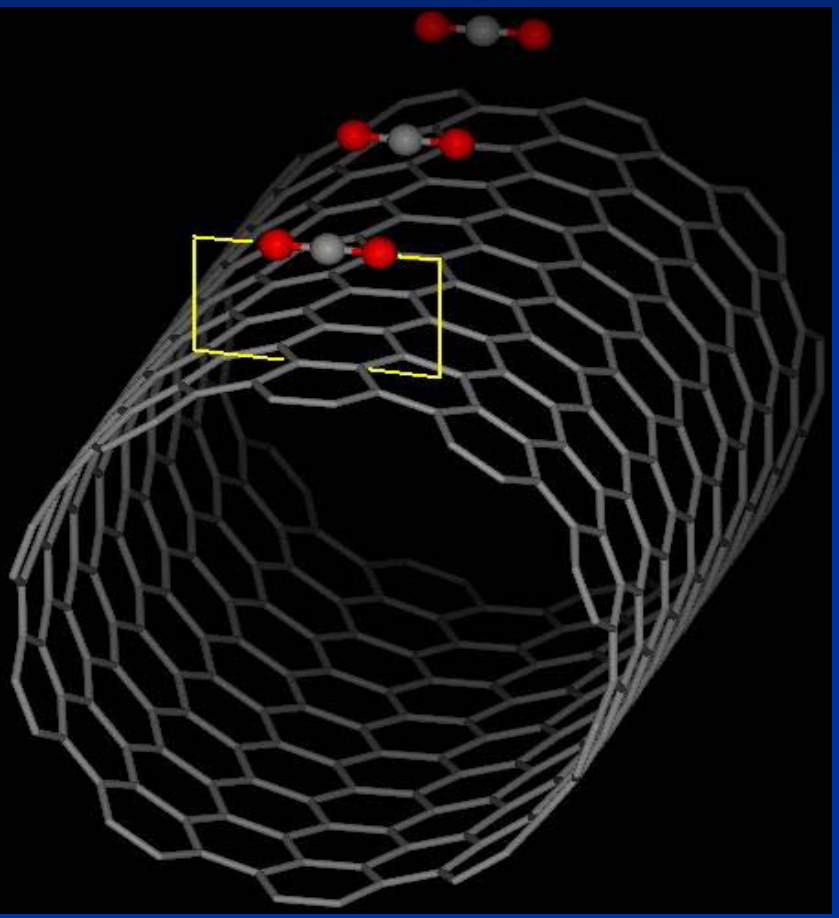


Bottom:

Snapshot of CO_2 adsorption in a large interstitial site of a bundle

From Matranga et al., *J. Phys. Chem. B*, in press

Density Functional Theory Calculations

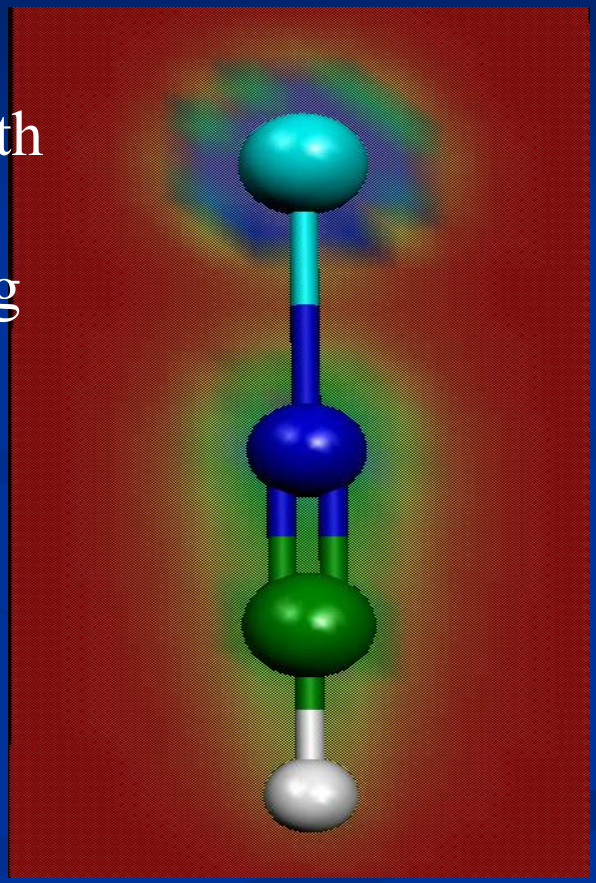


External CO_2

- Local density approximation
- Calculated binding energies and IR vibrational frequency shifts
- Binding energies and frequency shifts larger for internal adsorption
- Qualitative agreement with experiments (Byl & Yates)
- Experiment & theory paper submitted to *J. Chem. Phys.*

Conclusions

- Zn^{2+} and Cu^{2+} complexes HCN
- Linear N end-on geometry in agreement with previous theory and expt
- Zn^{2+} and Cu^{2+} energetics similar, suggesting roughly equivalent protection, in agreement with exptl data
- NCCN complexation? HCl formation?
- Role of H_2O?
- Synergy with TEDA? Both Zn^{2+} and Cu^{2+} complex with TEDA
- Weak cyanide complexation with TEDA



Conclusions (cont)

- Verified reaction paths of phosgene degradation by Zn^{2+}
- Energetics of AC complexation by Zn^{2+} compared to Cu2+ ions
- Verified stability of Cu-diamine complexation in alternative filtration media, reactivity of free amine
- Verified polymerization of CK

Future:

- Begin mapping energetics of AC,CK degradation in mixed (Cu,Zn,TEDA) environment to look at additive effects
- Water (humid environment)
- Alternative codes: ADF? Jaguar?
- Concurrent work on ethylene oxide adsorption in zeolites
- Nanotubes with Yim and Johnson (Pitt), exptl Yates (Pitt)

Acknowledgements

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